CALCIUM SULFOALUMINATE BELITE-PORTLAND CEMENT CONCRETE MIXTURES FOR RAPID HYDRATION AND STRENGTH GAIN

by

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Abstract

With infrastructure such as bridges, roadways, and runways needing constant maintenance and repair, more efficient and durable concrete materials are needed to ensure the safety of these structures. Ordinary portland cement (OPC) hydration and setting processes are too slow for these projects, which often run on tight schedules to minimize traffic interruptions, so accelerating admixtures, accelerators, are used to speed up the setting and strength gain. However, the most common and effective accelerator, $CaCl_2$ can promote the corrosion of steel reinforcement. Reinforced concrete structures rely on steel reinforcement for increased stability and tensile capacity, so losses due to corrosion can reduce the capacity and safety of structures. Calcium sulfoaluminate belite (CSAB) cement may provide a solution to this problem, while also being a greener and more sustainable cement binder. CSAB cement is a rapidly hydrating cementitious binder, setting in as little as 15 minutes without accelerators. This project will research the use of CSAB cements combined with OPC to determine if it is a viable option to replace accelerators while simultaneously reducing the amount of OPC used; while also providing similar or better properties. To test this, five mixes with different ratios of OPC to CSAB will be used to determine the best combination of materials to optimize properties. The design mixtures were tested to compare the setting time, compressive and tensile strength, resistivity (a measure of durability), and workability. It was hypothesized that CSAB can be use as an alternative to $CaCl_2$ accelerators, increasing early rates of strength gain while also providing durable concrete.

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Introduction

Concrete surrounds us wherever we look, but it does not last forever. With high-volume usage infrastructure such as bridges, roadways, and runways in need of repairs, development of rapid and reliable repair approaches for these structures is necessary. Although each agency's specification requirements differ, rapid repair techniques generally involve concrete with the following properties: rapid setting time, high early strength gain, corrosion resistance, and low shrinkage.[1]

With 400 psi flexural strength required to open roadways, the long set time of the typical OPC used in most structures can cause financial strain for high-volume structures.[2] To combat this, accelerators are used to speed up the hydration and initial set time of the concrete. This causes the concrete to gain strength more rapidly than in normal OPC systems.[3] However, the most common accelerator, $CaCl_2$, utilizes chlorides which can be harmful to reinforced concrete structures, with the chlorides introduced to the concrete increasing the risk of corrosion of the steel reinforcing bars.[3] Corrosion product build-up will lead to tensile forces inside the concrete and can lead to cracking and spalling that diminishes the integrity of the structure. These effects can be problematic when rapid repair projects need fast setting times but also have steel reinforcement that is susceptible to chlorides in the accelerator.

A possible solution to this scenario is to use CSAB cement. CSAB was discovered in China in the 1970's as a rapid setting cement.[4] Compared to OPC concrete, CSAB concrete can achieve similar strength in one day as OPC achieves after 28 days of hydration.[4] In addition to their rapid setting and strength gaining properties, CSAB cements are advantageous from a sustainability standpoint with reduced CO_2 emissions, and from a durability standpoint due to low shrinkage proclivity.[4]

With its rapid strength gain and low shrinkage properties, CSAB cements may provide a more sustainable and greener alternative to use of $CaCl_2$ accelerators in OPC concrete. However, little has been published regarding the properties and hydration kinetics of OPC-CSAB binary cement mixtures and the relationships between CSAB:OPC ratio and fresh and hardened properties. In addition, previous research has shown CSAB cements perform poorly with respect to chloride penetration – a significant concern for bridge deck concrete.[5] Thus, this research will explore the replacement of accelerators in OPC concrete with CSAB cement, and determine the effect of CSAB:OPC ratios on setting time, strength gain, and chloride penetration of concrete mixtures.

Materials

This study utilized concrete mixtures with five ratios of OPC and CSAB cements. An ASTM C150 Type I/II OPC (Fairborn Cement Company) and a CSAB cement (Buzzi Unicem USA) were utilized in all mixtures.[6] Gradations for the aggregates used in the mixes are shown in Figure 10 in the Appendix and include a 1" nominal #57 limestone and concrete sand from Columbus Builders Supply, in accordance with ASTM C33 requirements.[7] To control air content and slump, air entrainer (SikaControl® Air-160) and superplasticizer (Sika ViscoFlow®-2020) were used. For mixes with a high CSAB ratio, 99% citric acid (Alfa Aesar) was used as a retardant to delay the initial set time of the mixes. While acids reduce the pH in concrete, increasing the risk of corrosion, it was shown that citric acid used below 2% of total cement weight was found to not be problematic with corossion.[8]

Five mix designs were calculated using ACI 211.1-91 to generate the weight of water, cement, and aggregate per cubic yard, and cubic meter, as shown below in Table 1.[9] Each mix is listed by the percentage of OPC used, followed by the percentage of CSAB used in the mix (ie. 90/10 represents 90% OPC and 10% CSAB). Having mixes with a wide range in the OPC to CSAB ratio can give a better representation for how substituting more OPC for CSAB effects the mix design goal of 4000 psi in four hours, along with how other properties are affected. The air entrainer and superplasticizer dosages were found by using trial mixes. These mixtures were then scaled up for concrete for testing. Citric acid retarder doses were chosen based on vicat initial set time testing. The doses of citric acid that gave an initial set time of one hour were chosen for the concrete mixes. Fresh properties measured for the concrete mixtures, including slump and air content, are shown in Table 2.

Table 1: Mix design and properties of concrete batches used for tests.

Mix (volume)	Water lbs./cy (kg/m^3)	OPC lbs./cy (kg/m^3)	CSAB lbs./cy (kg/m^3)	Coarse lbs./cy (kg/m^3)	Fine lbs./cy (kg/m^3)	Citric Acid (wt% of CSAB)	Superpl-asticizer mL/100 kg	Air Entrainer mL/100 kg
100/0	337 (200)	871 (517)	0	1613 (957)	1015 (602)	0%	200	110
90/10	347 (206)	784 (465)	87 (52)	1613 (957)	1015 (602)	0%	569	110
70/30 + 1.5% cit.	347 (206)	610 (362)	261 (155)	1613 (957)	1015 (602)	1.5%	0	110
50/50 + 1.5% cit.	347 (206)	436 (259)	436 (259)	1613 (957)	1015 (602)	1.5%	74	140
0/100 + 1.0% cit.	337 (200)	0	871 (517)	1613 (957)	1015 (602)	1.5%	0	150

Table 2: Fresh concrete properties of each mix

Mix: OPC(%)/CSAB(%)	Slump (in.)	Air Content (%)
100/0	4”	6.5%
90/10	6 ½”	5.0%
70/30 + 1.5% cit	6”	3.5%
50/50 + 1.5% cit	5”	4.5%
0/100 + 1.0% cit	5 ½"	3.7%

Methodology

The preliminary testing is split into the testing done on the aggregates used and testing on the cement ratios. To ensure that the fine and coarse aggregates were suitable for concrete mixing, a sieve analysis was done following ASTM C33.[7] Specific gravity and moisture condition tests were done for the concrete mix design following ASTM C127 for coarse aggregate and ASTM C128 for fine aggregate.[10,11]

Vicat set time testing was performed to better understand the effect of varying ratios of OPC to CSAB for on initial and final set times following ASTM C191-18a.[12] For each OPC-CSAB mix, doses of citric acid varying from 0 – 1.5% of the CSAB cement weight were tested to obtain mixtures with 1-hour initial set time.

After completing the vicat testing, 0.3 cubic foot trial mixes were mixed following ASTM C192/192M-18.[13] The trial mixes were used to adjust the dosage of the air entrainer and superplasticizer. Once the mix designs were verified, they were scaled up for a 2 cubic foot mix to test compressive strength, tensile strength, resistivity, and chloride penetration. The concrete mixing followed ASTM C192/192M-18 and ASTM C31 to create the necessary 4”x8” cylinders for testing.[13,14] Samples were cured until the time of testing at 72 ºC and 100% RH. Compressive testing and resistivity were performed in triplicate at 4 hours, 1, 3, 7, 28, and 90 days following ASTM C39.[15] The compressive testing utilized the Forney compression actuator, ramping load application at a rate of 75 psi/s. Tensile testing was done in triplicate at 28 days of curing using the Forney compression actuator at a ramp rate of 4 psi/s following ASTM C496/496M-17.[16]

Chloride profiling on the mixes was done following ASTM C1556-11a and ASTM C1152/C1152M-04.[17,18] Once the samples had cured for 28 days they were cut using a chop saw 3” (75 mm) from the finished surface. The specimens were dried then sealed with a waterproofing paint to prevent intrusion of chlorides except through the top face of the cylinder. The samples were ponded in a saturated calcium hydroxide bath until their mass change was less than 0.1% in 24 hours, then placed in a container with NaCl exposure liquid. After 35 days the samples were removed from the salt solution and profile ground to the depths shown in Table 3, and called for by ASTM C1556. Profile grinding powder was dissolved in nitric acid then filtered, with solution chloride content determined by titration with silver nitrate using an ISE meter with silver-sulfide electrode.

Table 3: Recommended depth intervals for profile milling from ASTM C1556-11a.[17]

w/cm	Depth 1	Depth 2	Depth 3	Depth 4	Depth 5	Depth 6	Depth 7	Depth 8
0.35	0-1	1-2	2-3	3-5	5-7	7-9	9-12	12-16

Results and Discussion

Vicat initial and final set times for the final mixture retarder quantities are shown in Figure 1. The vicat testing goal was to have a mix with a 60 minute initial set time to allow for ample time to create all of the test cylinders, along with time to clean up. Figures 2-5 show the incremental increase of citric acid added by percentage of CSAB weight. The 50/50 + 1.5% cit mix, having the highest CSAB content of the OPC/CSA mixtures, was anticipated to have the highest retarder requirements and so was used as the baseline citric acid percentage used for the rest of the mixes with CSAB.

All of the mixes showed an increase in the initial and final set times when adding citric acid except for the 90/10. In Figure 2, the initial and final set times for the 90/10 mix were relatively consistent when changing the percent citric acid. This could be attributed to the low amount of citric acid relative to total cementitious materials content of the mixture and likely influence of the OPC cement. The 90/10 mixture utilized 360 grams of OPC cement, 40 grams of CSAB cement, and only 0.6 grams of citric acid retarder at 1.5%. This can be compared to 1.5% citric acid dosage used for the 0/100 mix, which used ten times the amount of citric acid, 6 grams.

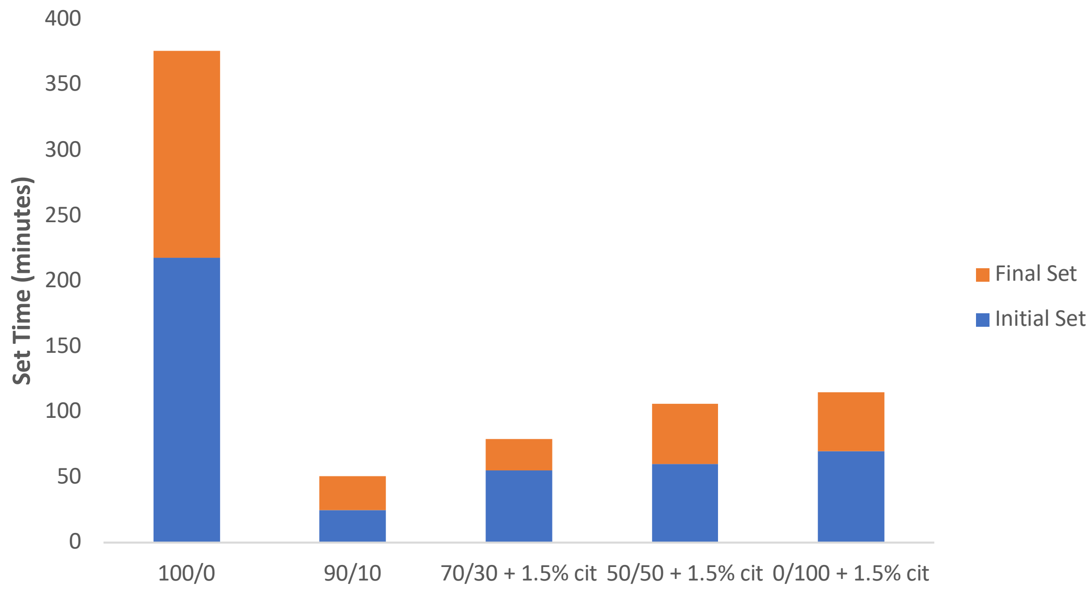

Figure 1: Initial and final set times for all finalized cement pastes, determined through vicat testing.

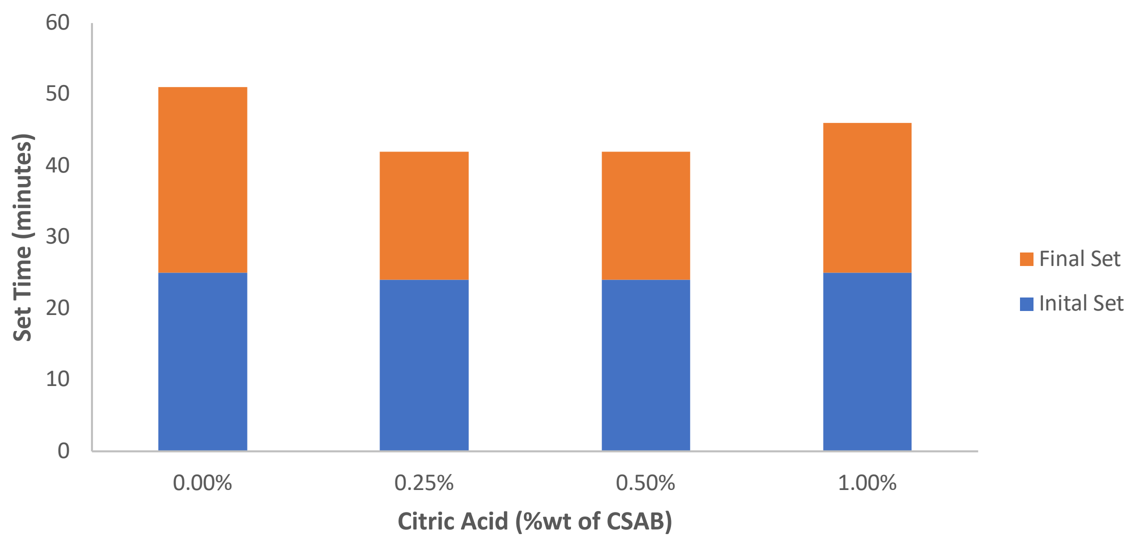

Figure 2: Set times for 90/10 cement pastes with different citric acid doses.

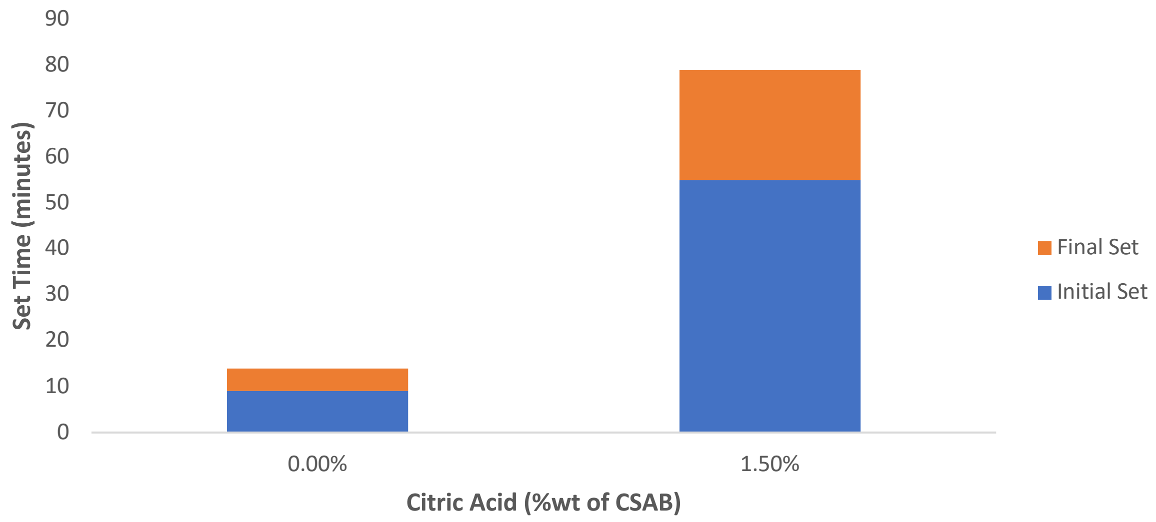

Figure 3: Set times for 70/30 cement pastes with different citric acid doses.

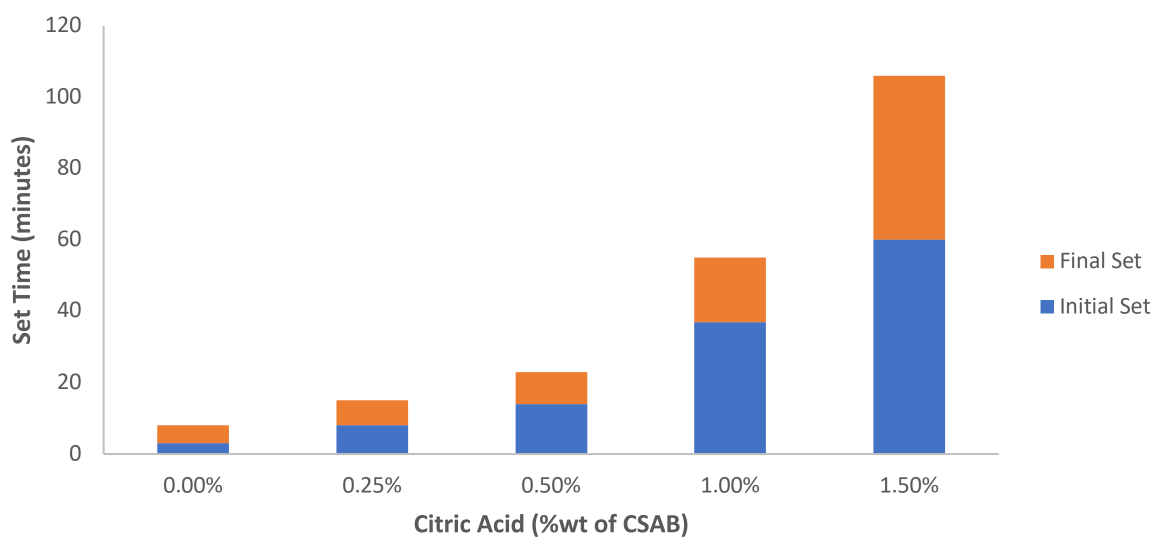

Figure 4: Set times for 50/50 cement pastes with different citric acid doses.

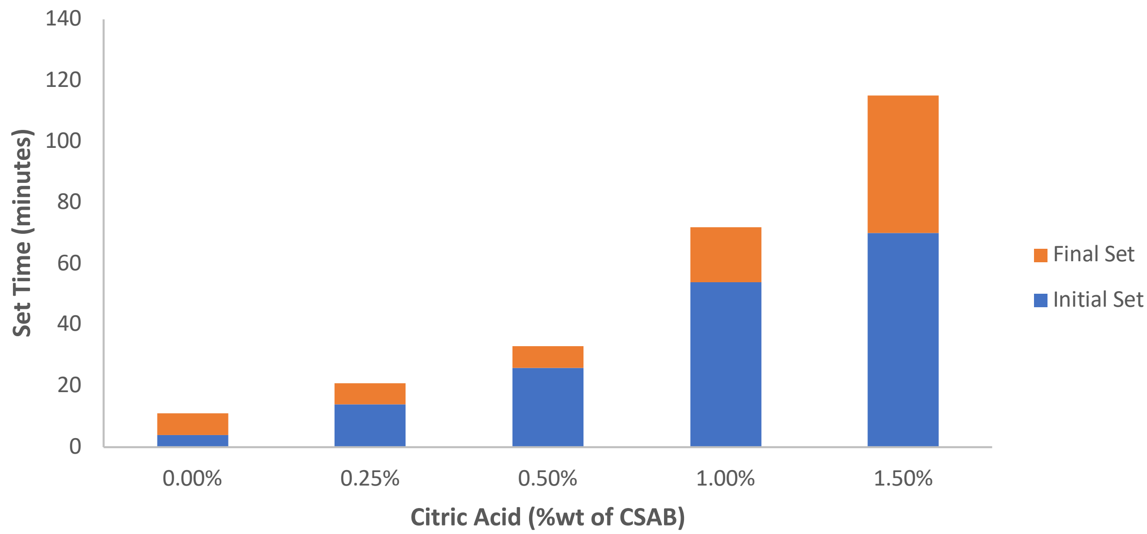

Figure 5: Set times for 0/100 cement pastes with different citric acid doses.

Results of the 4-hour compressive strength results are shown in Table 3. One of the original project goals was to create mixtures of OPC/CSAB which could qualify as rapid repair materials, able to obtain 4000 psi compressive strength 4 hours after initial mixing. The closest mix to the 4-hour goal of 4000 psi was the full CSAB 0/100 + 1.5% cit, followed by the 50/50 + 1.5% mixture. The CSAB cement generates faster early strength than OPC mixtures, and so, as a general trend, as the level of CSAB replacement decreased the early strength of the concrete also decreased.

Table 4: Average compressive strength of concrete cylinders at 4 hours.

Mix	Average 4 Hour Compressive Strength (psi)
100/0	Not Set
90/10	616
70/30 + 1.5% cit	571.33
50/50 + 1.5% cit	1575.67

0/100 + 1.5% cit	2986.5

Compressive strength test results are shown in Figure 6. All of the mixes containing CSAB had a higher 90-day strength than the OPC concrete. Additionally, the concrete samples that contained mixtures of OPC and CSAB continued to see increased rates of strength gain after 28 days of curing, while the 0/100 + 1.5% mix strength remained constant. This created a crossover effect, where all OPC/CSAB mixes to achieve 90-day strengths higher than the 0/100 + 1.5% mix.

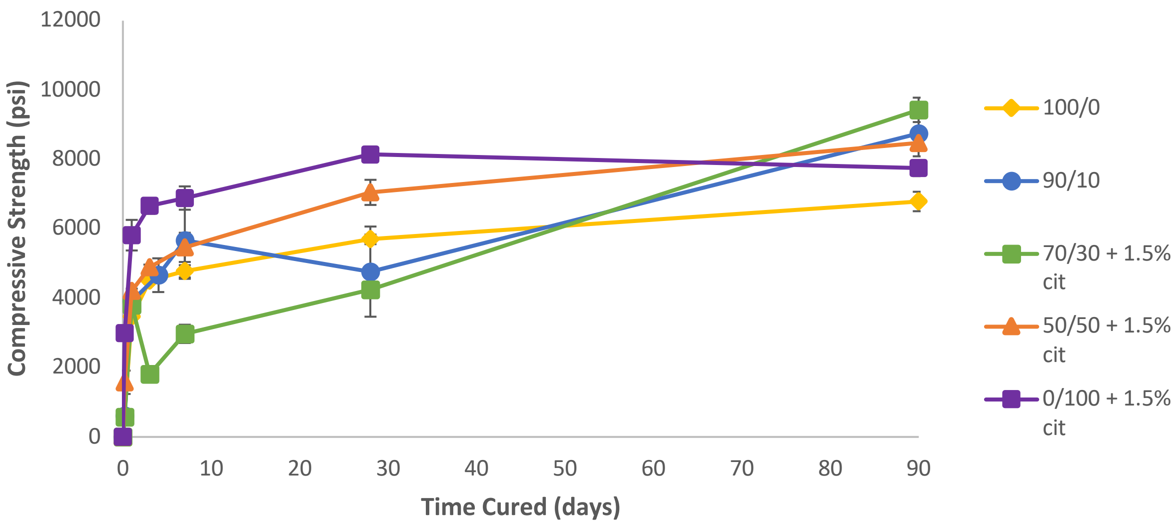

Figure 6: Average compressive strength of concrete cylinders over 90 days.

Tensile strength test results shown in Figure 7 show that the different mixes obtained similar tensile strengths as those of the OPC mix, with the exception of the 50/50 + 1.5% cit mix, which obtained a tensile strength approximately 200 psi greater than the OPC. In addition, typically tensile strength represents roughly 10-15% of the compressive strength.[19] As shown in

Table 4, all of the mixes meet this relationship except the 0/100 + 1.5% cit, which saw a relative reduction in $f_t/f'c$.

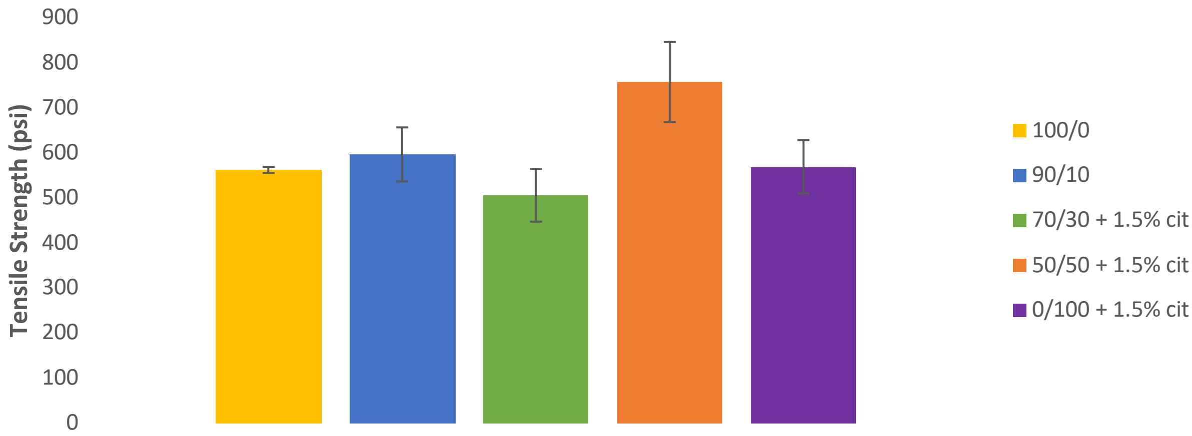

Figure 7: Average tensile strengths of concrete cylinders after curing for 28 days.

Table 5: Tensile strength divided by compressive strength

Mix	Tensile Strength / Compressive Strength
100/0	0.099
90/10	0.125
70/30 + 1.5% cit	0.119
50/50 + 1.5% cit	0.108
0/100 + 1.5% cit	0.070

Resistivity test results are shown in Figure 8. Resistivity has been correlated with durability and refinement and densification of pore structure for OPC mixtures, with higher values translating to more dense hydrated matrices, but standard relationships have not been determined for CSAB cement mixtures.[20] Previous research has also shown that CSA mixes have generally performed poorly with regards to chloride penetration.[5] Measurements for the 90/10 mix were mistakenly not measured until 28 days and so are not included in these results.

The 0/100 + 1.5% cit mix resistivity values were over an order of magnitude larger than the other mixes. Despite this, resistivity values for OPC/CSAB concretes did not directly correlate with CSAB substitution rate, and therefore may fit resistivity specification guidelines on use of resistivity to infer relative concrete durability. In addition, except for the 0/100 + 1.5% cit mix, which had an early peak followed by a slight decline in resistivity, all mixes generally show an increase in resistivity over time, suggesting increasing densification of all mixtures over the 90 day measurement period.

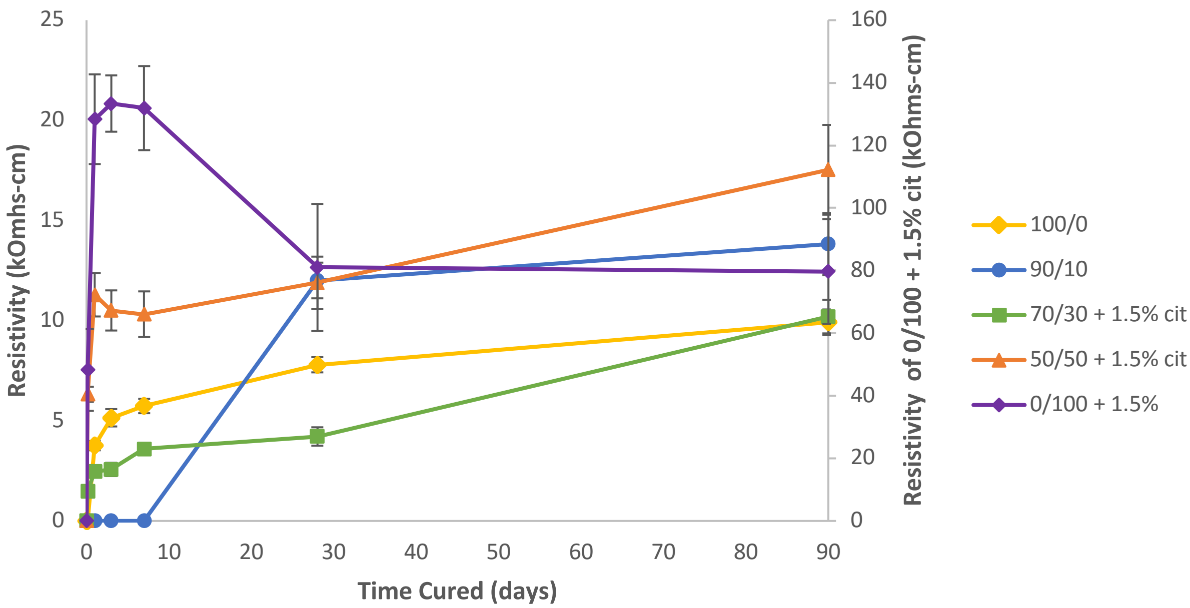

Figure 8: Average resistivity of concrete cylinders over 90 days.

The test result for the 100/0 chloride profiling is shown in Figure 9. Chloride profiling (Figure 9) determined the diffusion coefficient of the concrete to be 9.25×10^{-12} m^2/s. The values used in calculating the diffusion coefficient are shown in Table 7 in the Appendix. Diffusion coefficient provides a direct measurement of concrete resistance to chloride intrusion and allows for a correlation between resistivity values. Work is ongoing to determine diffusion coefficients for the 0/100 + 1.5% cit CSAB mixture and the 50/50 + 1.5% cit mixture.

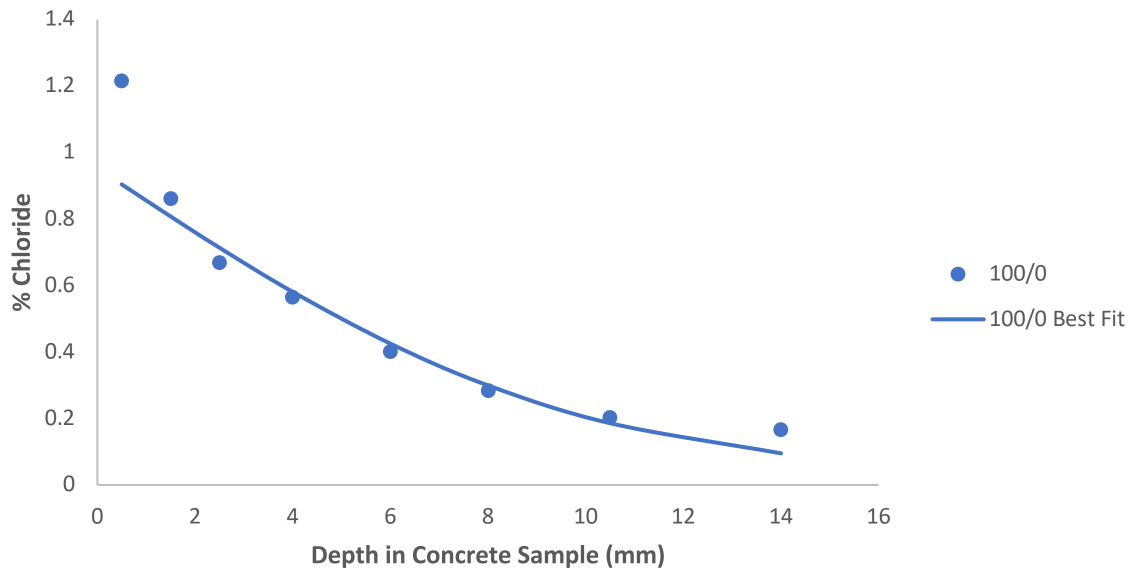

Figure 9: Chloride penetration into concrete samples.

Conclusions

The use of CSAB in concrete was successful in accelerating hydration and strength gain of concrete for time dependent projects. However, in this research work, no mix design was able to meet the goal of 4000 psi in 4 hours. However, the 0/100 + 1.5% cit mix did provide optimism that the goal is attainable with CSAB concrete. When lowering the doses of citric acid, the increased hydration of the concrete allows mixes to gain earlier strength. More research is needed on the other blends to see if they could attain the mix design goal with lower citric acid doses. Mixes with higher CSAB replacement seem best suited to obtain the mix design goal.

Lower CSAB replacement levels could be utilized for higher strength concretes - all mixes with CSAB replacement obtained higher 90-day strengths than the OPC concrete. Further research should be conducted to determine how the replacement levels effect the long-term (>90 days) strength development of the concrete.

The durability of CSAB has previously been shown to be a significant concern when compared to OPC concrete with respect to chloride penetration.[5] While the previous research shows that CSAB performs poorly with chloride penetration, the results from this research shows that the resistivity, and therefore durability, of two of the three OPC/CSAB concretes were higher than the 0/100 OPC concrete mixture, but were not so much higher as to suggest their values were artifacts of the CSAB system, which had very high resistivity despite known high diffusivity. Future testing of the diffusion coefficient of the mixes, will confirm if mixtures of OPC/CSAB concrete can provide resistance to chloride penetration, or if resistivity values do not correlate to chloride penetration in OPC/CSAB concrete.

After learning more about CSAB concrete and how blending CSAB with OPC affects the concrete properties it can be more safely and readily utilized for projects. Utilizing this greener cement may not only help the environment, but it may also improve upon certain properties of concrete we are using today.

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Appendix

Table 6: Average compressive strengths of concrete cylinders over 90 days.

Mix	4 hrs.	1 day	3 days	7 days	28 days	90 days
	Stress (psi)	Stress (psi)	Stress (psi)	Stress (psi)	Stress (psi)	Stress (psi)
90/10	616	3915	4663	5671.333	4765.667	8750.667
50/50 + 1.5% cit	1575.667	4211.5	4895	5465	7050.333	8477.667
70/30 + 1.5% cit	571.333	3807.333	1810.667	2972	4248.5	9126
100/0	---	3477.667	4506	4775	5695.333	6787.333
0/100 + 1.0% cit	2986.5	5816.333	6656	6886.667	8147.667	7743.667

Table 7: Average resistivity values of concrete cylinders over 90 days.

Mix	4 hrs.	1 day	3 days	7 days	28 days	90 days	Average
90/10	---	---	---	---	12.004	13.821	12.913

50/50 + 1.5% cit	6.325	11.292	10.508	10.321	11.888	17.529	11.310
70/30 + 1.5% cit	1.492	2.463	2.571	3.596	4.217	10.204	4.090
100/0	---	3.758	5.150	5.738	7.796	9.917	6.472
0/100 + 1.0% cit	48.288	128.363	133.363	131.896	81	79.721	100.438

Table 8: Error function calculations for diffusion coefficient

Cs (mass %)	**Ci (mass %)**	**Da (m^2/s)**	**t (days)**	**Sum $(Error)^2$**
0.953	0.039	9.25E-12	35	1.17E-02

x (mm)	**Measured Values**	**Predicted Values**	**Error (Meas. - Pred.)**	**$Error^2$**
0.5	1.215	0.904		
1.5	0.862	0.808	0.054	2.98E-03
2.5	0.668	0.714	-0.046	2.09E-03
4	0.564	0.581	-0.017	2.81E-04
6	0.401	0.425	-0.024	6.11E-04
8	0.283	0.299	-0.016	2.74E-04
10.5	0.203	0.186	0.017	2.91E-04
14	0.167	0.095	0.072	5.16E-03

Table 9: Requirement for fine aggregates from ASTM C33.

Sieve	% Passing
3/8	100
#4	95-100
#8	80-100
#16	50-85
#30	25-60
#50	5-30
#100	0-10
#200	0-10
Pan	0

Table 10: Percent of concrete sand passing through each sieve.

Sieve	% Passing
3/8	100.00
#4	99.75
#8	91.30
#16	62.11
#30	30.77
#50	10.7
#100	2.90
#200	0.81
Pan	0.00

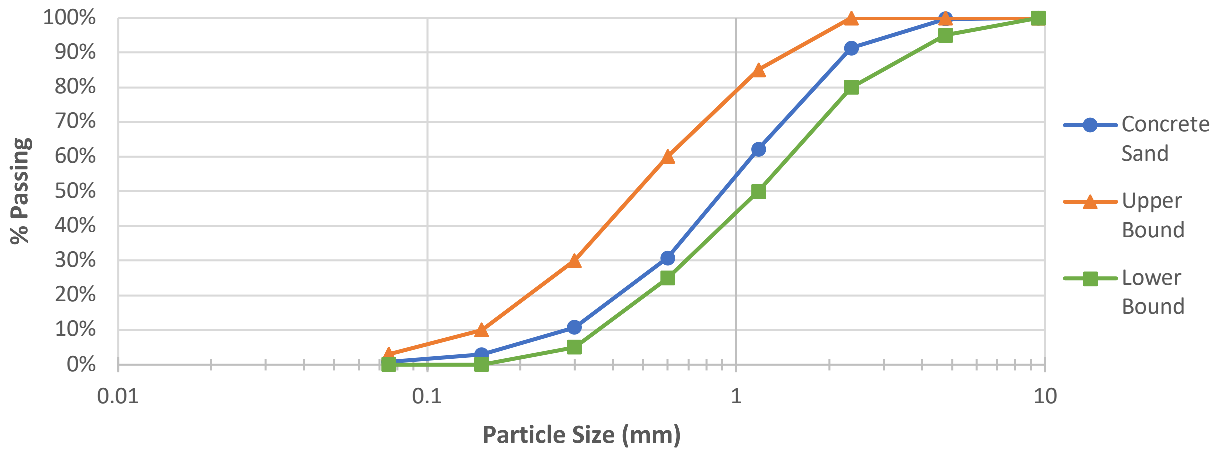

Figure 10: Percent passing of concrete sand with bounds from ASTM C33 [2].

Table 11: Average tensile strengths of concrete cylinders after curing for 28 days.

Mix	**28 hrs.**
	Stress (psi)
90/10	579
50/50 + 1.5% cit	758
70/30 + 1.5% cit	506.333
100/0	562.667
0/100 + 1.0% cit	569.667